Niobium-Tantalum Content of Ilmenite-Rich Black Sands from Walikale (North Kivu, Democratic Republic of Congo)

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INTRODUCTION.

Mineralogical and geochemical characterization of alluvial deposits is a prerequisite for both the exploration and the exploitation of valuable sedimentary occurrences, such as heavy mineral deposits, and for the interpretation of sediment provenance. Mineralogical characterization comprises two main factors, namely mineral assemblage and geochemical composition of mineral groups, or even individual mineral grains (Bernstein et al., 2008). For long time, it has proven useful to concentrate efforts on the characterization of the heavy mineral fraction because this fraction includes a group of diverse minerals, reflecting a large range in source rock compositions, and because almost all valuable mineral raw materials, -existing in recent sediments-, such as ilmenite, zircon, garnet, and monazite, are found in this heavy fraction.

Niobium is a crucial element as an alloying element in steels and in superalloys for aircraft turbine engines, being in greatest demand in industrialized countries. It is critical in the aerospace, energy, and transportation industries. Some other substitute elements are available, but, in most applications, they are less desirable. Tantalum is a key metal in the current electronics industry. It is mainly consumed for the production of tantalum capacitors utilized in mobile phones, laptop computers, digital cameras, as well as automotive and medical uses. During the 1999-2001 IT boom, a tantalum supply crunch stimulated Ta resources exploration and a re-evaluation of known old Ta deposits around the globe. Although exploration activities have decreased since then and several projects were abandoned due to a decrease in tantalum prices, some large scale projects are still running.

Despite the classical obtaining of these two elements from "coltan" (columbo-tantalite ores), the improvement in the technology for Nb-Ta recovery from non-conventional sources address the exploration not only to some Nb-Ta rich deposits, also to alternative resources (Adetunji, 2005; Amuda et al., 2007). The conventional method to benefit tantalite mineral is the gravity separation technique due to the density of Ta-Nb minerals which allows concentration with other heavy metals. However, at now, the focus is the concentration of multiconstituents of tantalum bearing minerals with a view to generating economic value for the secondary ore concentrates (TiO_2, MnO_2, ZrO_2, SnO_2, Fe_2O_3, etc.) in the tantalum bearing minerals.

For many years, the composition of ilmenite has been used as exploration guide for diamondiferous kimberlites and placers. Four main ilmenite ore types have been identified around kimberlitic areas: a) Mg-rich ilmenites, b) Fe-rich ilmenites, c) Mn-rich ilmenites and d) near stoichiometry ilmenites related to different genetic origins (Robles-Cruz et al., 2009).

The main aim of the present work is to characterize two different Nb-Ta bearing ilmenite black sands deposits, from Walikale mining district (Democratic Republic of Congo, North Kivu province), exploring its geochemical and mineralogical features. Samples are called Walikale-1 and Walikale-2, and were collected in alluvial deposits of Walikale River. The second one is not far from the well-known Walikale tin-bearing mining district and the first one is collected around hundred kilometres downstream.

ANALYTICAL TECHNIQUES.

X-Ray Diffraction.

X-ray diffraction analyses were carried out at controlled temperature of 25ºC, using Cu Kα radiation (40 kV and 40 mA) using a Bruker diffractometer, type D8-Advance. The XRD spectra were recorded using theta/2theta geometry, collecting data in the range (2θ) between 4° and 60° with a step scan of 0.05°, 1s per step. The evaluation of the spectra was made by using the Diffrac.Suite™ software and identification of chemical compounds (when they were present) by the use of PDF database.

fig 1. Ilmenite sand grains from Walikale aluvial deposits

Wavelength X-Ray Fluorescence.

Bulk mass samples were analyzed using a WDXRF instrument (Bruker S4 Explorer) equipped with an Rh anticathode X-ray tube (50 kV, 20 mA); four analyzer crystals (OVO-B, OVO-55, LiF 200 and PET) and a flow proportional counter for light element detection and a scintillation counter for heavy elements.
In this work, analyses were made in vacuum atmosphere to avoid signal losses by air absorption. In a first stage, all the samples were analyzed to obtain the whole spectra at standard conditions, which were studied to determine elemental composition, sensitivities and detection limits. Secondly, a fundamental parameters

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semiquantitative model (standardless mode) was designed improving the elemental peaks signal for each element to be determined. Both activities were carried out using the software (Spectra Plus, Bruker/AXS) linked to the equipment.

μ-Energy Dispersive X-Ray Fluorescence.

We use a benchtop energy-dispersive X-ray spectrometer (XDV-SD model, Helmut Fischer GmbH, Sindelfingen, Germany to study the geochemistry of isolated single grains. It consists of a microfocus tungsten anode X-ray tube, -able to operate at fixed voltage of 10, 30 and 50 kV and within a range of 0.1 to 1 mA of intensity- and a Si-Pin semiconductor detector. A colour video microscope allows selection and viewing of the irradiated area with up to 45x magnification. Four collimators with different diameters (0.1, 0.3, 1 and 3 mm) are also available in the spectrometer to irradiate selected areas.

The instrument is controlled by the WinFTM® - v.6.20 software, which is also used both for the spectra acquisition and for the spectral data treatment. This software is based on the physical principles detailed in the Roessiger & Nensel (2003) work. It also can do evaluation by using quantitative standard based models or by standard free fundamental parameters method. For the intended purpose of the present work we use a motorized XYZ stage, allowing obtaining spectral data on different modes: a) point by point, obtaining an spectrum on each point, b) step scan mode, obtaining one spectrum per fixed steps along transects on sample surface and, c) continuous scan, delivering only one spectrum representative of large scanned areas, minimizing the non-homogeneity of the sample surface, and d) programmed gridding, to obtain elemental mapping.

On such a way μ-XRF becomes a fully automated technique for the determination of chemical and physical properties of a large number of individual particles, thus enabling the precise and accurate geochemical investigation on individual mineral grains as well as their compositional variation). The method, however, does not provide all of the important information as obtained by standard petrographic microscopy such as grain colour, birefringence, etc. and therefore the method cannot distinguish between polymorphs with identical chemical compositions. However, up to now, μ-XRF has been not extensively applied in those sedimentological studies that rely on mineralogical information obtained from a large number of individual mineral particles.

RESULTS.

From the X-ray diffraction plots of both ilmenite sands we can conclude a high content of ilmenite in these black sand deposits. Some minor quantities of quartz and grossular were found in the sample Walikale 1 and quartz, anatase, ortochlase and muscovite were identified in the sample Walikale 2.

	Walikale-1	Walikale-2
TiO_2	47.8	48.1
Fe_2O_3	32.7	38.4
MgO	9.45	0.22
Al_2O_3	1.13	2.16
SiO_2	3.15	4.98
Cr_2O_3	2.64	—
MnO	0.85	3.22
ZnO	0.015	0.132
ZrO	0.032	0.126
SnO_2	—	0.061
WO_3	—	0.075
Nb_2O_5	0.298	0.225
Ta_2O_5	0.057	0.051

Table 1. Bulk analysis of ilmenites by WDXRF. Results in %

The bulk geochemical results exhibit a contrasting chemistry for both samples. Walikale 1 is a Mg-ilmenite also rich in chromium whilst Walikale 2 can be considered as Mn-rich ilmenite (pyrophanite).

From the point of view of niobium and tantalum content both investigated ilmenites exhibit contents over the mean of análisis reported in literature elsewhere.

The statistical analysis of mineral grains shows a different degree of homogeneity for both samples as reflected by their coefficient of variation (COV). Walikale 1 reported slightly higher -and constant- contents of Nb and Ta. Walikale 2 exhibit a noticeable heterogeneity in the Ta content, despite the mean average is nearly the same for both samples.

Item 1	Walikale1			Walikale2	
	Nb_2O_5	Ta_2O_5		Nb_2O_5	Ta_2O_5
n	165	165		140	140
min(%)	0.094	0.003		0.058	0.006
max(%)	0.657	0.177		0.489	0.387
mean(%)	0.295	0.057		0.215	0.053
stdev	0.11	0.03		0.05	0.06
C.O.V.(%)	36.6	54.7		21.2	102.7

Table 2. Statistical results from μ-XRF analysis of single ilmenite grains. n:number of analysis, stdev: standard deviation, C.O.V.: coefficient of variation.

REFERENCES.

Adetunji, A.R. (2005): Development of an efficient process for the recovery of tantalum compounds from Nigeria's tantalite ores. Unpublished Ph.D thesis, Obafemi Awolowo University, Ile-Ife, Nigeria

*Amuda, M.O.H., Esezobor, D.E. Lawal, G.I. (2007): Adaptable Technologies for Life-Cycle Processing of Tantalum Bearing Minerals. J. of Minerals & Materials Characterization & Engineering, **6**, 69-77.*

*Bernstein, A., Frei, D., McLimans, R.K., Knudsen, C., Vasude, V.N. (2008): Application of CCSEM to heavy mineral deposits: Source of high-Ti ilmenite sand deposits of South Kerala beaches, SW India. J. Geochem. Explor., **96**, 25–42.*

*Robles-Cruz, S.E., Watangua, M., Isidoro, L., Melgarejo, J.C., Galí, S., Olimpio, A. (2009): Contrasting compositions and textures of ilmenite in the Catoca kimberlite, Angola, and implications in exploration for diamond. Lithos, **112S**, 966–975.*

*Roessiger, V. & Nensel,B. (2003): Non Destructive Analysis of Gold Alloys Using Energy Dispersive X-Ray Fluorescence Analysis. Gold Bull., **36**, 125-137.*